OPTIMAL MANUFACTURING PROCESS OF SELF-HEALING MICROCAPSULES FOR DAMAGE REPAIR TECHNIQUES IN POLYMER COMPOSITES

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Abstract
The purpose of this study is to investigate the optimal manufacturing process for microcapsules that contains a liquid healing agent. Microcapsules were fabricated by an in-situ encapsulation method with shell walls made of melamine, urea, and formaldehyde. The molar ratio of constituents was fixed. A mesh and the pH of the reaction were considered as processing parameters. The morphology of the microcapsules was observed by an optical microscope and a field emission scanning electron microscope. The size distribution and cumulative distribution of microcapsules were measured by a particle size analyzer. The weight changes of microcapsules and their constituents were investigated by a thermogravimetric analyzer. According to the results, suggested methodology enables microcapsules with acceptable thermal stability, uniform size, and improved storage capability.

1. Introduction

Polymeric composites are widely applied in aerospace, automobile, shipbuilding, and civil engineering industries. Such composites are susceptible to invisible and undetectable damage induced by mechanical and/or thermal loadings. Much effort has been paid to the development of damage repair techniques for polymeric composites [1-3]. Self-healing polymeric composites, inspired by biological systems [4,5], utilize a microencapsulated healing agent and dispersed catalysts within the polymeric matrix to repair damage autonomously. When polymeric composites are damaged, a crack propagates to break microcapsules and the healing agent is then released into the crack plane by capillary action. When the healing agent contacts a catalyst, in-situ polymerization occurs to prevent further crack growth and repairs the damage.

In order to apply self-healing technique for damage repair of polymeric composites successfully, microcapsules should satisfy several requirements: (1) microcapsules have to be

thermally stable and prevent diffusion of the healing agent during the shelf life, (2) the shell wall of microcapsules must be robust enough to remain during the fabrication of the polymeric composites, and (3) microcapsules should have enough adhesion with the polymer matrix to ensure that microcapsules rupture upon polymeric composite fracture [6-8]. Therefore, an optimal manufacturing methodology is necessary to obtain reliable microcapsules with thermal stability, uniform size, and improved storage capability.

In this study, the optimal manufacturing process for microcapsules that contain the healing agent was investigated. Microcapsules were fabricated by an in-situ polymerization where the shell wall was made of melamine (M), urea (U), and formaldehyde (F). During the manufacturing process for microcapsules, the molar ratio of these shell wall constituents was fixed. A mesh and pH of the reaction were considered as processing parameters. The morphology and shell wall thickness of microcapsules were observed by an optical microscope and a field emission scanning electron microscope (FE-SEM). The size distribution and cumulative distribution of microcapsules were measured by a particle size analyzer (PSA). The weight changes of microcapsules and their constituents were also investigated by a thermogravimetric analyzer (TGA).

2. Experimental

2.1. Manufacturing process of microcapsules

Microcapsules containing the healing agent were manufactured by an in-situ polymerization of the constituents such as melamine, urea, formaldehyde, endo-dicyclopentadiene (DCPD), sodium dodecyl sulfate (SDS), and polyvinyl alcohol (PVA). The melamine, urea, and formadehyde, supplied by Sigma-Aldrich, USA, were used for the microcapsule shell wall. The endo-DCPD, supplied by Acros, USA, was used as the healing agent. SDS and PVA, supplied by Junsei, Japan, were used as an emulsifier and a stabilizer. In this study, the molar ratio of shell wall constituents (M:U:F) was set to 3:1:8.5 as the optimal reaction conditions [8]. Fig. 1 shows the experimental set-up for manufacturing microcapsules. The manufacturing process for microcapsules was as follows: (1) aqueous solution of 0.5 wt% SDS and 6.3 wt% PVA were heated at 80 °C for 20 min and 120 min on a hot plate with a magnetic stirrer, respectively and then cooled down to 25 °C, (2) mixture of 3.84 g melamine and 7.01 g formaldehyde solution (37 wt% in H_2O) with 70 g deionized water was heated at 70 °C for 25 min until a clear solution was obtained and then cooled down to 25 °C, (3) 0.61 g urea was dissolved with 30 g deionized water in 600 ml reaction beaker at 25 °C and its solution was agitated with a three blade low shear mixing impeller (PL010, Daihan Scientific, Korea) at 500 rpm for 5 min, (4) prepared solution of melamine and formaldehyde was added in the reaction beaker and agitated at 500 rpm for 10 min, (5) 30 g SDS solution was added in the reaction beaker and agitated at 500 rpm for 5 min, (6) 30 g PVA solution was added into the reaction beaker and agitated at 500 rpm for 5 min, (7) 30 g endo-DCPD was put into the reaction beaker covered with an aluminum foil and agitated at 500 rpm while being heated to 86 °C at a heating rate of 2 °C/min, (8) after reaching 86 °C, the mixture was agitated at 500 rpm for 320 min, (9) 10 g deionized water was added after 90 min and 5 g deionized water was refilled every 30 min to replace the evaporated water from the reaction beaker during isothermal reaction and continuous agitation, and (10) microcapsules were decanted on the paper filter and then vacuum filtered three times with distilled water for rinsing. After drying for 720 min at 25 °C, microcapsules were easily separated via shaking, representing a successful manufacturing process.

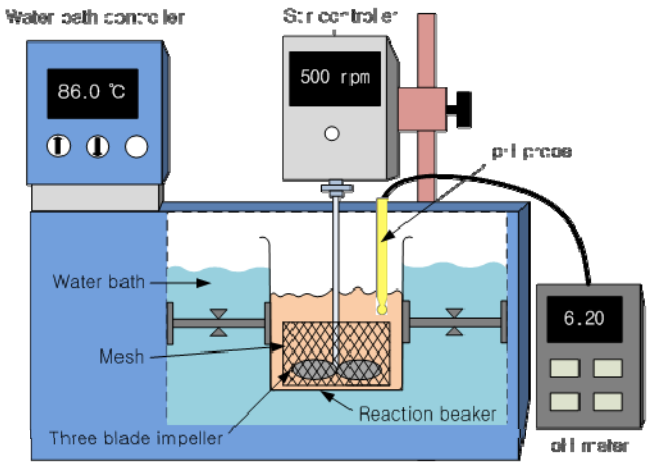


Figure 1 Experimental set-up for manufacturing microcapsules.

To obtain microcapsules with uniform size and thermal stability during the manufacturing process, a mesh was used to stabilize the internal flows in the reaction beaker, which reduced the cavitation around the axle of a three blade low shear mixing impeller via high agitation speed. Fig. 2 shows the internal flows in the reaction beaker without and with a mesh when agitation speed was set to 500 rpm. The internal flows in the reaction beaker with a mesh were more stable than those without a mesh, which resulted in less cavitation around the axle of a three blade low shear mixing impeller.

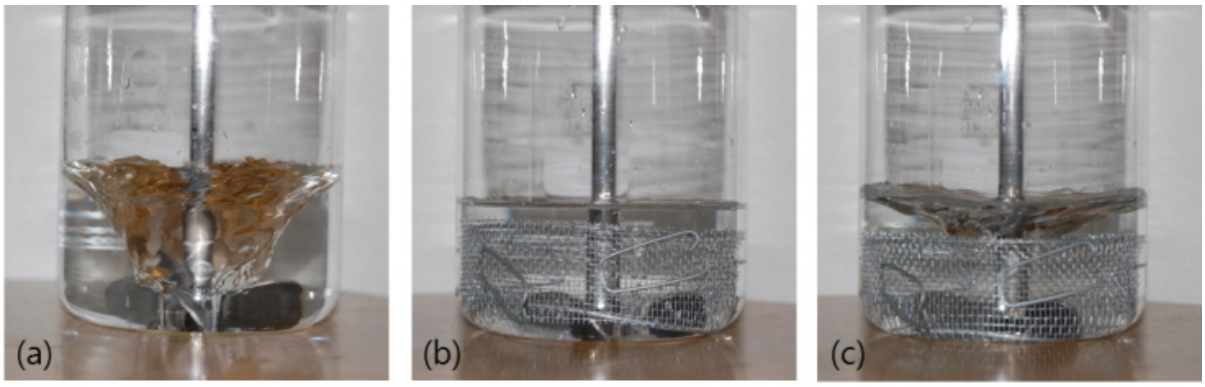


Figure 2 Internal flows in the reaction beaker: (a) internal flows without a mesh agitating at 500 rpm, (b) internal flows with a mesh before agitating, and (c) internal flows with a mesh agitating at 500 rpm.

2.2. Characterization of the microcapsules

The morphology and shell wall thickness of microcapsules were examined by an optical microscope (ICSN-4H-102, Sometech, Korea) and a field emission scanning electron microscope (JSM6500F, Jeol, Japan). In order to prepare the samples for shell wall thickness of microcapsules, adhesive coated plate spreading microcapsules was put into liquid nitrogen for freezing and then held at 25 °C for 12 hr after being cut with a razor blade. The size and size distribution of microcapsules were measured by a particle size analyzer (Mastersizer 2000, Malvern Instrument, UK). The weight changes of microcapsules and their constituents were investigated by a thermogravimetric analyzer (TGA Q500, TA Instruments, USA) upon continuously heating from 30 °C to 600 °C at a heating rate of 10 °C/min. The thermal stability of microcapsules was also examined upon heating from 30 °C to 150 °C at a heating

rate of 10 °C/min and then kept at an isotherm condition for 120 min before continuously ramping up to 600 °C at a heating rate of 10 °C/min.

3. Results and Discussion

Fig. 3 shows the photographs of microcapsules observed by an optical microscope. Three of them were manufactured with a mesh under the pH control from pH 5.8 to pH 6.2 and one was manufactured without a mesh at pH 6.2. Figure (a) was for pH 5.8 with a mesh, (b) was for pH 6.0 with a mesh, (c) was for pH 6.2 with a mesh, and (d) was for pH 6.2 without a mesh. The size of microcapsules was very uniform and the diameter of microcapsules was approximately 140 μm when a mesh was used during the manufacturing process. The size of microcapsules manufactured without a mesh was less uniform than those manufactured with a mesh and the diameter of microcapsules was approximately 220 μm. Also, microcapsules manufactured without a mesh have more debris than those manufactured with a mesh. When the pH of the reaction was lower, the reaction occurred rapidly, resulting in more agglomeration.

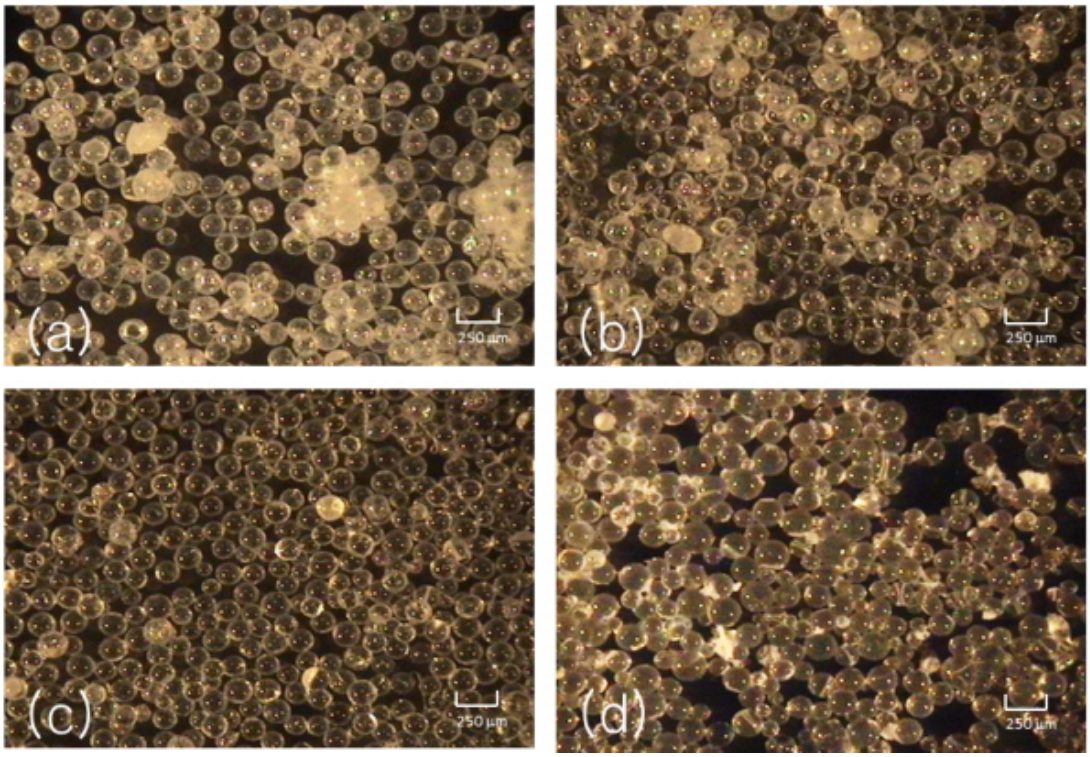


Figure 3 Photographs of microcapsules manufactured with and without a mesh under the pH control: (a) microcapsules manufactured with a mesh at pH 5.8, (b) microcapsules manufactured with a mesh at pH 6.0, (c) microcapsules manufactured with a mesh at pH 6.2, and (d) microcapsules manufactured without a mesh at pH 6.2.

Fig. 4 shows the size distribution and cumulative distribution of microcapsules manufactured with and without a mesh under the control of pH 6.2 via a particle size analyzer. The size distribution of microcapsules manufactured with a mesh was more uniform and less scattered than those manufactured without a mesh. When a mesh was used during the manufacturing process, the diameters of microcapsules in terms of surface weighted mean and volume weighted mean were 136 μm and 144 μm, respectively. The cumulative distributions of microcapsules were 103 μm at 10 %, 140 μm at 50 %, and 191 μm at 90 %. When a mesh

was not used, the diameters of microcapsules in terms of surface weighted mean and volume weighted mean were 212 μm and 228 μm, respectively. The cumulative distributions of microcapsules were 156 μm at 10 %, 220 μm at 50 %, and 311 μm at 90 %. Microcapsules manufactured with a mesh were smaller and more uniform than those manufactured without a mesh.

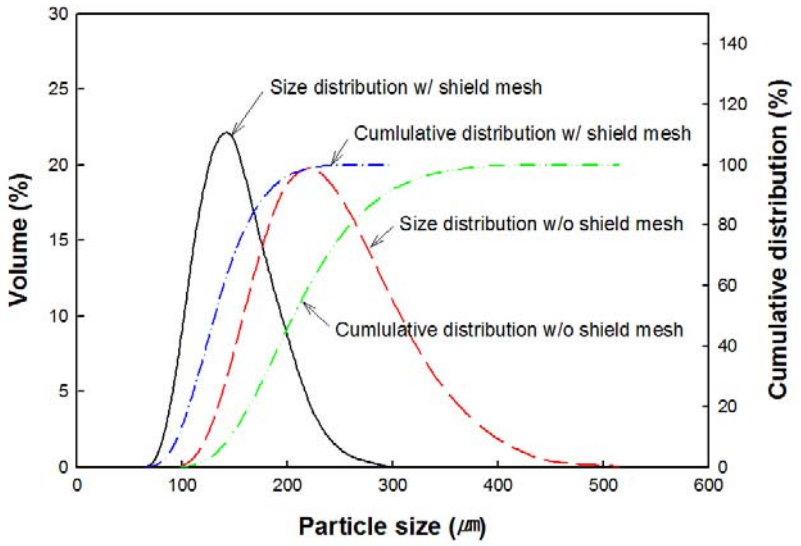
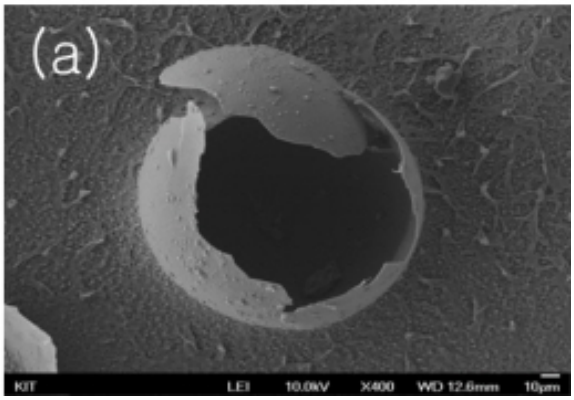


Figure 4 Size distribution and cumulative distribution of microcapsules manufactured with and without a mesh.

Fig. 5 shows the surface morphology of microcapsules manufactured with and without the pH control from pH 5.8 to pH 6.2. All microcapsules were manufactured with a mesh at an agitation speed of 500 rpm. Figure (a) was the configuration of microcapsules manufactured at pH 6.2. Figure (b) was the surface morphology of microcapsules manufactured without pH control and figures (c)-(e) were the surface morphology of microcapsules manufactured with the pH control from pH 5.8 to pH 6.2. The surface morphology of microcapsules manufactured without the pH control was rough and porous. When the pH of the reaction was controlled, the surface morphology of microcapsules was denser than those manufactured without the pH control. The shell wall thickness of microcapsules was measured from the surface morphology. The shell wall thickness of microcapsules manufactured without the pH control was 637 nm. The shell wall thickness of microcapsules manufactured with the pH control was 642 nm for pH 5.8, 620 nm for pH 6.0, and 593 nm for pH 6.2. The shell wall thickness of microcapsules was approximately between 590 nm and 640 nm, even though different pH of the reaction was applied.



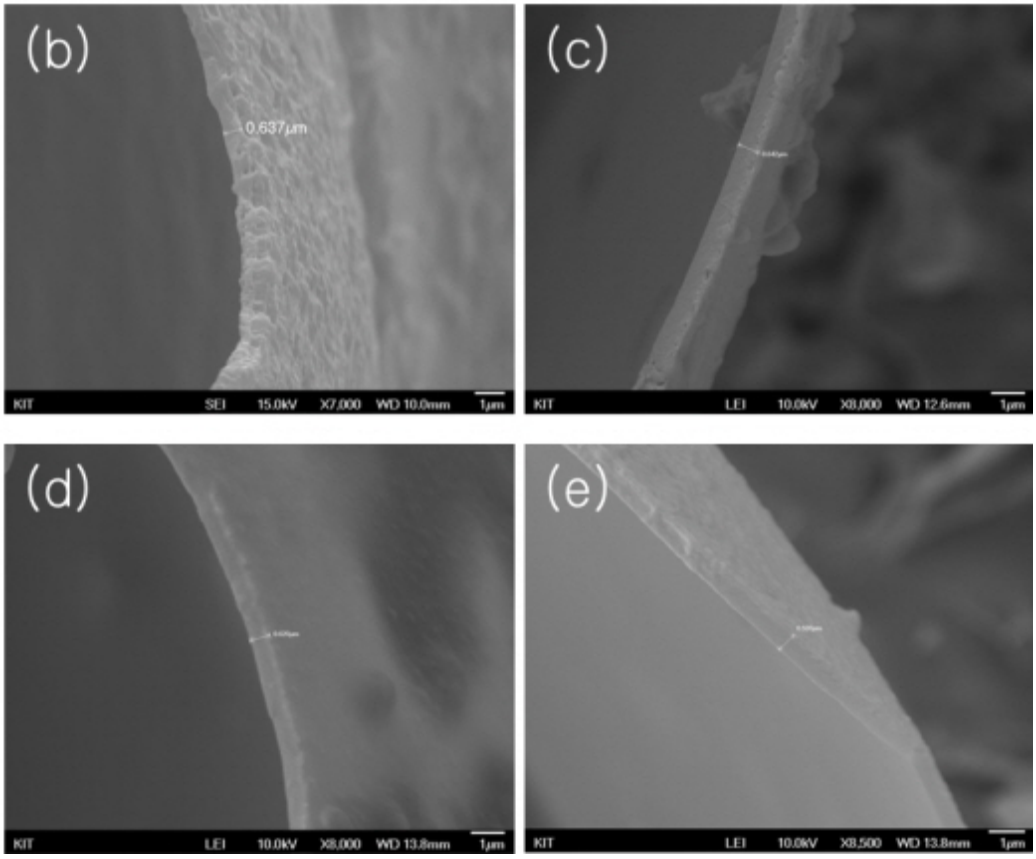


Figure 5 Surface morphology of the microcapsule manufactured at 500 rpm with and without the pH control: (a) configuration of the microcapsule manufactured at pH 6.2, (b) shell morphology of the microcapsule manufactured without the pH control, (c) shell morphology of the microcapsule at pH 5.8, (d) shell morphology of the microcapsule at pH 6.0, and (e) shell morphology of the microcapsule at pH 6.2.

Fig. 6 shows the TGA results of microcapsules manufactured with a mesh by varying the pH of the reaction as well as their constituents, where the temperature was continuously heating from 25 °C to 600 °C. As shown in the figure, sudden weight drop occurred for urea and melamine starting at 135 °C and 220 °C, respectively. The ending temperatures for a sudden weight drop were 325 °C for both constituents. Microcapsules manufactured with a mesh revealed a similar trend in weight drop. As the temperature increased from 25 °C to 220 °C, microcapsules manufactured under the pH control of pH 5.8, pH 6.0, and pH 6.2 reduced their weight gradually to 71.5 %, 70.4 %, and 74.3 %, respectively. As the temperature increased to 325 °C, microcapsules manufactured under the pH control of pH 5.8, pH 6.0, and pH 6.2 reduced their weight suddenly to 5.2 %, 2.7 %, and 7.8 %, respectively. Although the amount of weight drop was slightly different at starting and ending temperatures, the change in weight drop between the starting and ending temperatures was almost 67 % for microcapsules manufactured with a mesh given different pH controls. As microcapsules manufactured with a mesh maintained the temperature of healing agent at 220 °C, above boiling temperature of DCPD, microcapsules were found to be thermally stable. Also, as starting and ending temperatures of microcapsules for a weight drop were the same as those of melamine, melamine was found to have a significant effect on the thermal stability of microcapsules. However, the starting and ending temperatures for the weight drop of microcapsules manufactured without a mesh were 60 °C and 230 °C, respectively, which were related to the surface morphology of the shell wall examined by a scanning electron microscope.

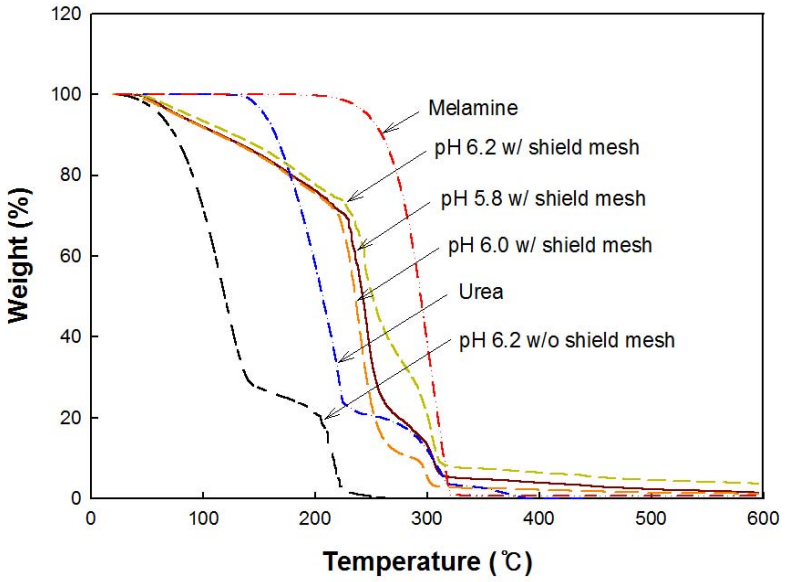


Figure 6 TGA results of microcapsules manufactured with a mesh by varying the pH of the reaction as well as their constituents under continuous heating.

Fig. 7 shows the TGA results of microcapsules manufactured with a mesh by varying the pH of the reaction under continuous heating with isotherm condition. The temperature was heating up from 25 °C to 150 °C and held isothermally for 120 min before continuing to heat up 600 °C. The amount of weight drop was 15 % from 25 °C to 150 °C and an additional 46.7 % during the isotherm condition for microcapsules manufactured at pH 5.8. For microcapsules manufactured at pH 6.0 and pH 6.2, the amount of weight drop was 20 % in temperatures between 25 °C and 150 °C. During the isotherm at 150 °C for 120 min, the amount of weight drop was 14.6 % for microcapsules manufactured at pH 6.0 and 15.6 % for microcapsules manufactured at pH 6.2.

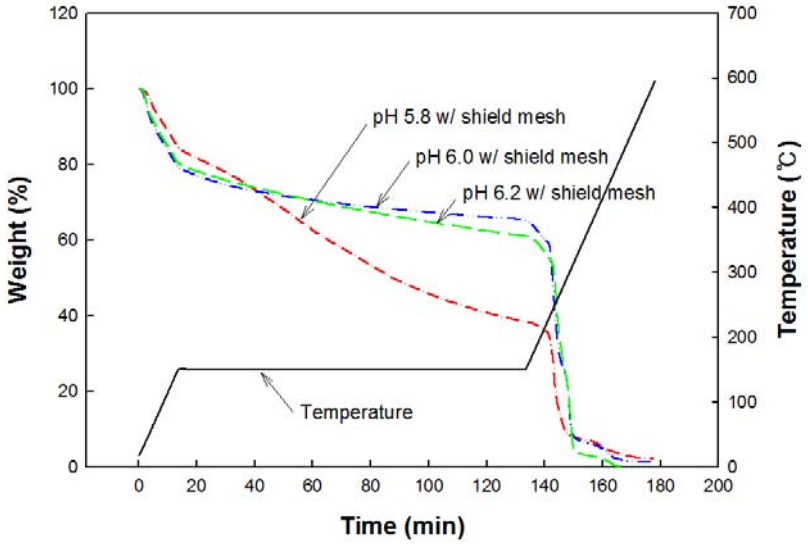


Figure 7 TGA results of microcapsules manufactured with a mesh by varying the pH of the reaction under continuous heating from 25 °C to 600 °C with isotherm condition at 150 °C for 120 min.

4. Conclusions

The optimal manufacturing process for microcapsules containing the healing agent was investigated. Microcapsules were manufactured by an in-situ polymerization and the shell wall was made of melamine, urea, and formaldehyde. While fixing the molar ratio of shell wall constituents, a mesh and the pH of the reaction were considered as processing parameters. When applying pH 6.2 of the reaction and 500 rpm of the agitation speed, microcapsules manufactured with a mesh have less debris and more uniform size than those manufactured without a mesh. The diameters of microcapsules manufactured with a mesh were approximately 140 μm and microcapsules were easily separated via shaking. The surface morphology of microcapsules manufactured under the pH control of the reaction was denser and shell wall thickness was approximately between 590 nm and 640 nm. The amount of weight drop was approximately 15.6 % during the isotherm at 150 °C for 120 min. Therefore, the suggested methodology enables acceptable microcapsules with thermal stability, uniform, size, and improved storage capability.

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References

[1] A. Yousefpour, M. Hojjati, J. P. Immarigeon. Fusion bonding/welding of thermoplastic composites. *Journal of Thermoplastic Composite Materials*, 17:303-341, 2004.
[2] J. Paul and R. Jones. Repair of impact damaged composites. *Engineering Fracture Mechanics*, 41:127-141, 1992.
[3] K. B. Zimmerman and D. Liu. An experimental investigation of composite repair. *Experimental Mechanics*, 36:142-147, 1996.
[4] C. M. Dry and N. R. Sottos. Passive smart self-repair in polymer matrix composite materials. In *Conference on recent advances in adaptive and sensory materials and their applications*, 438:444, 1992.
[5] S. R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, and S. R. Sriram, E. N. Brown, and S. Viswanathan. Autonomic healing of polymer composites. *Nature*, 409:794-797, 2001.
[6] M. R. Kessler, N. R. Sottos, and S. R. White. Self-healing structural composite materials. *Composites Part A*, 34(8):743-753, 2003.
[7] X. Liu, J. K. Lee, S. H. Yoon, and M. R. Kessler. Characterization of diene monomers as healing agents for autonomic damage repair. *Journal of Applied Polymer Science*, 101:1266-1272, 2006.
[8] X. Liu, X. Sheng, J. K. Lee, and M. R. Kessler. Synthesis and characterization of melamine-urea-formaldehyde microcapsules containing ENB-based self-healing agents. *Macromolecular Materials and Engineering*, 294:389-396, 2009.